Monitoring of Decabromodiphenylether in the European Environment: Results of the First Five Years (2005-2009)

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Introduction

Decabromodiphenylether (BDE209) is currently being monitored in environmental matrices in a program that covers a period of 10 years (2005-2014). The ultimate aim is to study time trends of this chemical in sparrowhawk and glaucous gull eggs, sewage sludge and sediments from various locations in Europe. Locations in Western Europe were selected to see if a stewardship program installed by the bromine industry would be effective. While it is too soon to establish reliable time trends (only 3-5 data points until now), the results of the first five years of this program can now be presented.

Materials and Methods

The program makes use of bird's eggs, sewage sludge and sediment samples from Western Europe (Table 1). Sparrowhawk (*Accipiter nisus*) egg samples (UK) are being used to monitor diffuse sources at remote locations in the UK, while glaucous gull (*Larus hyperboreus*) egg samples from the Arctic region (Norway) are giving information on exposure in areas that may be affected by long-range transport of BDE209. Sewage sludge was sampled in various sewage treatment plants (STPs) in The Netherlands and the UK. Sediments samples have been taken in various estuaries in the UK: Mersey (Liverpool Bay and Boillin Point, Manchester), Tees, Thames and Humber, in the Western Scheldt (Belgian border), The Netherlands, in the Liffey, Dublin harbour, Ireland, and in estuaries of the rivers Elb and Ems (Germany), and Seine, France.

Table 1. Sampling plan

	Sparrow hawk egg	Glaucous gull egg	Sewage sludge	Sediment
Number of sites	2	1	12	10
Samples per site	12 (total both sites)	12	3 composite samples (week)	4 (composite)
Number of samples per sampling year	12	12	36	40
Sampling frequency	Annual	Annual	Biennial	Biennial
Total samples in 10-year programme	108	108	180	200

Extraction, cleanup and analysis. Analyses were carried out under the specific conditions for BDE209 analysis as described in de Boer and Wells (2001). The extract was dried with sodium sulphate and extracted by Soxhlet with hexane:acetone 3:1 (v/v) with ^{13}C-labelled BDE209 and BDE58 (2,3,3',5'-tetrabromodiphenylether) added as internal standards. Extracts were cleaned with an acid silica column, followed by a further clean-up step on a silica column. The final extracts were concentrated to 600 µl, and analysed by GC/ECNI-MS. A 15 m DB-5 column (internal diameter 0.2 mm, film thickness 0.1 µm) was used for the BDE209 measurements. Two blank samples and one internal reference material were analysed in each series of twelve samples. Quantification of BDE209 was based on the fragments m/z 486.4 and 484.4. The limit of detection was set at three times the noise level and the limit of quantification (LOQ) was set at three times the LOD. The total lipid contents of eggs were determined by the Bligh and Dyer method (1959). BDEs 28, 47, 99, 100, 153 and 183 were also screened in two eggs of each species each year (data not shown).

Results and Discussion

The work completed so far has shown BDE209 to be present at a range of concentrations from <LOD to higher values, with the lowest values found in glaucous gulls, followed in increasing order by sparrow hawk eggs , Dutch sewage sludge, most sediments, UK sludge, Liverpool Bay sediments, Western Scheldt and Mersey and sediments. Glaucous gull eggs showed extremely low concentrations of decaBDE, with a high number of non-detects in 2006 (8 out of 12 eggs) compared to the first study year when there were only 2 non-detects (Fig.1). Other studies have reported BDE209 concentrations in wild predator birds. A study of birds sampled in China [Chen *et al*. 2007] reported a higher frequency of BDE209 detects (79.4% of samples) with average BDE209 levels well above detection limits: *e.g.* sparrow hawk liver 254 ng/g lipid weight (lw) and in common kestrel liver 2,870 ng/g lw. This indicates that in the tissues of certain bird species in some environments, BDE209 concentrations can be much higher than what we found in the eggs in our study. Lindberg *et al.* [2004] reported BDE209 concentrations in wild peregrine falcon eggs ranging from <7 to as high as 430 ng/g lw. All the concentrations detected in the glaucous gull eggs in the present study were well below the values reported by Lindberg *et al.* [2004].

BDE209 was detected in 10 of the 12 sparrow hawk eggs analysed in the first sampling year and in the single egg collected in 2006. In the eleven samples where BDE209 was detected, it was present at higher concentrations than in the glaucous gull egg samples. The BDE209 concentration ranged from 2.4 to 36 ng/g lipid weight in sparrow hawks, (Fig. 2). The sparrow hawk egg data fall in the lower end of the concentration range found by Lindberg *et al.* [2004].

The average BDE209 levels measured in sludge from the six Dutch STPs were in the range of 755 to 1,482 ng/g on an organic carbon (OC) basis, while in the UK and Ireland, the average levels were considerably higher, ranging from 2,388 to 20,000 ng/g OC (Figure 3). The reason for this difference is unknown, although it may have to do with consumer habit differences between the countries. Possibly, clothes and carpets in the UK are more heavily flame-retarded. The BDE209 concentrations at Dutch STPs with substantial industrial input such as Eindhoven, Bath and Kralingseveer, including in some cases input from textile industries were not significantly higher on a dry weight (dw) basis than those from Dutch STPs with little to no input from such industries. BDE209 concentrations reported in an earlier study [see de Boer *et al*. 2006] at several of the same STPs as this study showed similar values on dw basis in effluents and sludge (*e.g.* Eindhoven 350 ng/g dw in centrifuged effluent particulate matter). The size of the community (rural vs. urban) which the facilities serve does not correlate to the BDE209 levels found.

BDE209 was detected at all sites in almost all sediment samples, covering a wide range of concentrations over the sites (Fig. 4). The lowest levels of BDE209 were detected at the sites on the Seine, Elb, Ems, Outer Humber and Thames, where average concentrations ranged from about 70 to 700 ng/g OC. Tees and Dublin Harbour sediments had higher concentrations, 4,410 and 3,190 ng/g

OC respectively. The highest BDE209 concentrations were measured at the sampling sites on the River Mersey (average 54,100 ng/g OC), at Liverpool Bay (40,600 ng/g OC) and the Western Scheldt (53,300 ng/g OC). BDE209 data in sediments from some of the same sites are available from the Diffchem study [Anon., 1997]. The organic-carbon normalized BDE209 concentrations in the Seine, Elb, Ems and Mersey were in the same range as the concentrations reported in sediments from the same locations in the Diffchem study (sampled in 1995). On the other hand, in the Diffchem report, the mean BDE209 concentration (of three samples measured) in Western Scheldt sediment is 200 ng/g dw, which is considerably lower than the concentrations found in this study (Fig. 3)

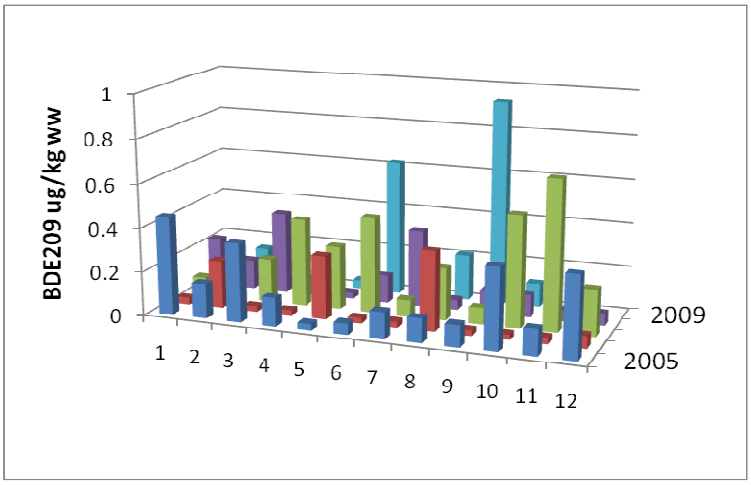

Figure 1. BDE209 concentrations in glaucus gull eggs from Bear Island, Norway in µg/kg wet weight.

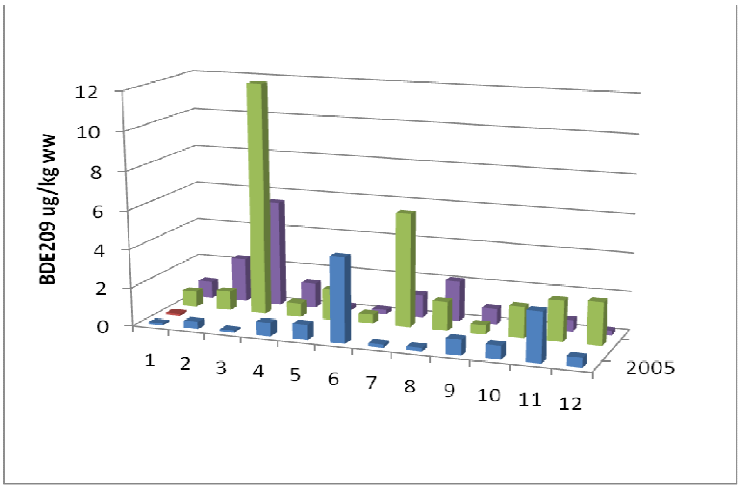

Figure 2. BDE209 concentrations in sparrow hawk eggs from the UK, in µg/kg wet weight.

Obviously, more data points are needed for establishing reliable time-trends, in particular for the bird egg data as the combination of low concentrations and organisms placed high in the food chain causes substantial differences between individual samples.

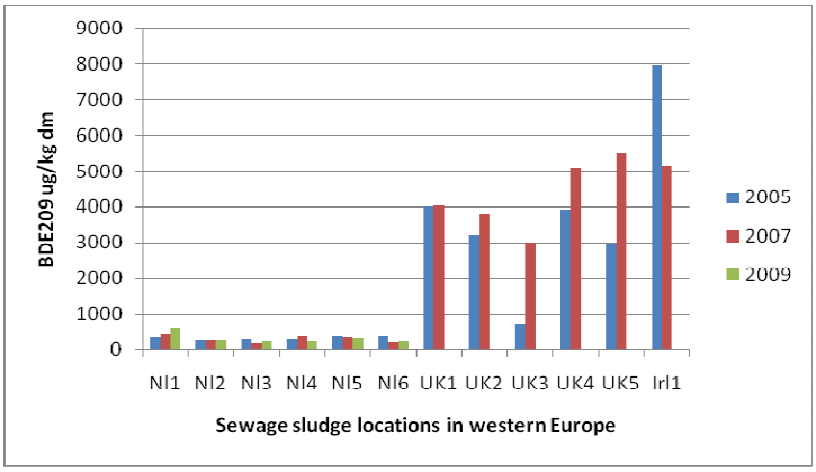

Figure 3. BDE209 concentrations in sewage sludge, in µg/kg dry matter.

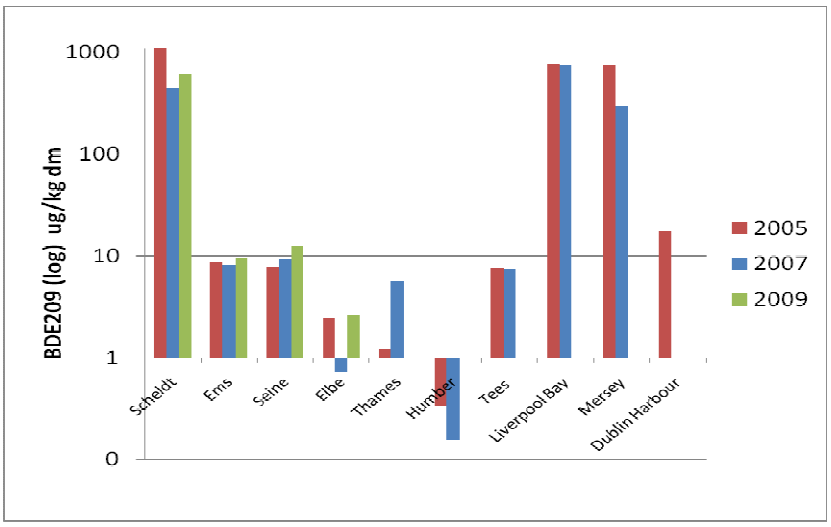

Figure 4. BDE209 concentrations in sediments, in µg/kg dry matter.

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